methoxyphenoxy group of (III) – it should be noted that there are contacts shorter than van der Waals radii between the two parts in (I). These contacts, which are not strictly determined either by cyclic structure or by two atoms being bonded to the same atom, are O(2)$\cdots$C(10) 2·86 Å, C(9)$\cdots$C(10) 2·93 Å and O(5)$\cdots$C(7) 3·13 Å. These short non-bonding contacts must be due to favourable packing of the crystal with this conformation of the molecule, as no favourable intramolecular contacts are seen here such as the contact O(5)$\cdots$C(7) observed for (III) (Destro & Saccarello, 1983).

To some extent the bonding geometry around C(8) in (I) must be caused by short non-bonding intramolecular contacts and the crystal-packing forces. For that reason, care has to be taken when trying to predict the behaviour of (I) in solution, but keeping this in mind one would predict that the O(2)—C(8) bond, which is somewhat longer than the two other O—C bonds around C(8), should be the most susceptible to hydrolysis according to the hypothesis proposed by Ankersen, Nielsen & Senning (1989). This assumption is supported by the fact that (I) yields 51·1% aspirin (IV) and 48·9% salicylic acid (V) upon hydrolysis at pH = 7·4 and a temperature of 310 K (Ankersen & Senning, 1989), indicating that the hydrolysis follows either path 1 or 3 of the reaction scheme.

The conformation of the half boat of the aspirin moiety of (I) is closer to ideality (see Table 2) than the equivalent part of (III) (Destro & Saccarello, 1983), probably because of the more flexible linkage

between the two parts of the molecule causing fewer unfavourable short non-bonding intramolecular contacts.

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Structure of Tetraphenylphosphonium Decahydro-8-hydroxy-9-methyl-6-carba-*nido*-decaborate(1 −) Ethanol Solvate

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Abstract. $C_{24}H_{20}P^+.C_2H_{14}B_9O^-.C_2H_5OH$, $M_r = 536\cdot89$, triclinic, $P\bar{1}$, $a = 10\cdot253$ (3), $b = 10\cdot971$ (2), $c = 14\cdot326$ (5) Å, $\alpha = 89\cdot96$ (2), $\beta = 81\cdot22$ (3), $\gamma = 88\cdot74$ (2)°, $V = 1592\cdot2$ (8) Å^3, $Z = 2$, D_m (flotation) $= 1\cdot122$, $D_x = 1\cdot120$ g cm^{-3}, λ(Mo $K\alpha$) $= 0\cdot71073$ Å, $\mu = 1\cdot06$ cm^{-1}, $F(000) = 568$, $T = 293$ K, $R = 0\cdot058$ for 3982 observed independent reflections. The novel monocarbadecaborane anions have OH ligands attached to the B8 atoms. The oxygen of the OH group is involved in O—H$\cdots$O hydrogen bonding with the ethanol solvent. Two anions and two alcohols form a centrosymmetric 'dimer'. Mean O1$\cdots$O2 = 2·763 (4) Å, mean O—H$\cdots$O = 174 (5)°.

Introduction. Crystals of the title compound were prepared in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences by the specific stepwise degradation reaction of a reactive isomer (r-$C_2B_{10}H_{13}$) (Plešek, Jelínek, Štíbr & Heřmánek, 1989). The removal of one B and one C atom from

$C_{24}H_{20}P^+.C_2H_{14}B_9O^-.C_2H_5OH$

Table 1. *Fractional coordinates and B_{eq} values (Hamilton, 1959) for non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
P	0·51574 (7)	0·25646 (6)	0·76622 (5)	2·97 (2)
C11	0·6157 (3)	0·2519 (3)	0·6520 (2)	3·54 (7)
C12	0·6218 (4)	0·3522 (3)	0·5923 (2)	4·8 (1)
C13	0·7064 (5)	0·3473 (5)	0·5076 (3)	6·5 (1)
C14	0·7786 (4)	0·2445 (5)	0·4804 (3)	6·7 (1)
C15	0·7738 (4)	0·1443 (4)	0·5391 (3)	6·1 (1)
C16	0·6932 (3)	0·1482 (3)	0·6256 (2)	4·80 (9)
C21	0·6236 (2)	0·2233 (2)	0·8501 (2)	2·87 (6)
C22	0·7397 (3)	0·2883 (3)	0·8453 (2)	4·07 (8)
C23	0·8250 (3)	0·2652 (3)	0·9089 (2)	4·42 (9)
C24	0·7971 (3)	0·1763 (3)	0·9759 (2)	3·91 (8)
C25	0·6837 (3)	0·1118 (3)	0·9811 (2)	4·14 (8)
C26	0·5963 (3)	0·1349 (3)	0·9192 (2)	3·58 (7)
C31	0·4374 (3)	0·4031 (2)	0·7883 (2)	3·22 (7)
C32	0·4719 (3)	0·4815 (3)	0·8557 (2)	4·16 (8)
C33	0·4041 (4)	0·5916 (3)	0·8724 (3)	5·2 (1)
C34	0·3016 (4)	0·6224 (3)	0·8235 (3)	5·5 (1)
C35	0·2689 (3)	0·5443 (3)	0·7558 (3)	4·9 (1)
C36	0·3353 (3)	0·4350 (3)	0·7384 (2)	4·06 (8)
C41	0·3849 (3)	0·1486 (2)	0·7751 (2)	3·23 (7)
C42	0·2756 (3)	0·1662 (3)	0·8444 (2)	3·91 (8)
C43	0·1744 (3)	0·0848 (3)	0·8535 (3)	4·8 (1)
C44	0·1809 (4)	−0·0137 (3)	0·7949 (3)	5·3 (1)
C45	0·2870 (4)	−0·0322 (3)	0·7277 (3)	5·6 (1)
C46	0·3903 (3)	0·0480 (3)	0·7158 (2)	4·39 (9)
B1	0·1696 (4)	0·1520 (4)	0·1819 (3)	5·0 (1)
B2	0·1092 (4)	0·2735 (4)	0·1209 (3)	4·8 (1)
B3	0·0591 (3)	0·2659 (3)	0·2426 (3)	3·94 (9)
B4	0·1766 (4)	0·1856 (3)	0·3037 (3)	4·4 (1)
B5	0·2816 (4)	0·2408 (5)	0·1064 (3)	5·5 (1)
C6	0·2329 (3)	0·3727 (4)	0·1150 (2)	5·1 (1)
B7	0·1189 (4)	0·4041 (3)	0·1936 (3)	4·06 (9)
B8	0·1481 (3)	0·3447 (3)	0·3182 (2)	3·71 (8)
B9	0·3072 (4)	0·2742 (4)	0·3190 (3)	4·6 (1)
B10	0·3223 (4)	0·1728 (4)	0·2206 (3)	5·0 (1)
O1	0·0864 (3)	0·4071 (2)	0·3993 (2)	5·20 (7)
C	0·3924 (5)	0·2749 (5)	0·4011 (4)	6·6 (1)
O2	0·1029 (2)	0·4078 (2)	0·5898 (2)	5·23 (7)
C1	0·0385 (5)	0·3061 (4)	0·6396 (3)	6·3 (1)
C2	0·0962 (7)	0·1888 (5)	0·6029 (5)	8·1 (2)

Table 2. *Molecular geometry*

(a) Bond distances (Å) in tetraphenylphosphine

P—C11	1·794 (3)	P—C31	1·789 (3)
P—C21	1·785 (3)	P—C41	1·798 (3)
C11—C12	1·388 (4)	C31—C32	1·385 (4)
C11—C16	1·392 (4)	C31—C36	1·392 (4)
C12—C13	1·380 (5)	C32—C33	1·384 (4)
C13—C14	1·360 (7)	C33—C34	1·384 (6)
C14—C15	1·380 (7)	C34—C35	1·381 (5)
C15—C16	1·381 (5)	C35—C36	1·369 (5)
C21—C22	1·394 (4)	C41—C42	1·390 (4)
C21—C26	1·386 (4)	C41—C46	1·389 (4)
C22—C23	1·375 (5)	C42—C43	1·374 (5)
C23—C24	1·371 (4)	C43—C44	1·365 (5)
C24—C25	1·366 (4)	C44—C45	1·351 (5)
C25—C26	1·373 (5)	C45—C46	1·382 (5)

(b) Bond distances (Å) in carbaborane cage and ethanol

B1—B2	1·745 (6)	B4—B8	1·772 (5)
B1—B3	1·800 (5)	B4—B9	1·713 (5)
B1—B4	1·796 (6)	B4—B10	1·765 (5)
B1—B5	1·761 (6)	B5—C6	1·520 (6)
B1—B10	1·758 (6)	B5—B10	1·895 (6)
B2—B3	1·742 (5)	C6—B7	1·528 (5)
B2—B5	1·777 (5)	B7—B8	1·962 (5)
B2—C6	1·681 (5)	B8—B9	1·791 (5)
B2—B7	1·786 (6)	B8—O1	1·406 (4)
B3—B4	1·807 (5)	B9—B10	1·785 (6)
B3—B7	1·752 (5)	B9—C	1·569 (7)
B3—B8	1·760 (5)	O2—C1	1·440 (5)
		C1—C2	1·469 (7)

(c) Torsion angles (°)

B8—O1—H(O1)—O2	179 (2)	C1—O2—H(O2)—O1	102 (6)

(d) Hydrogen interactions (Å and °)

X—H⋯Y	X⋯Y	X—H	H⋯Y	X—H⋯Y
O1—H(O1)⋯O2^i	2·766 (4)	0·79 (5)	1·98 (5)	173 (5)
O2—H(O2)⋯O1	2·760 (4)	0·93 (6)	1·83 (6)	175 (5)

Symmetry code: (i) $-x, y - 1, z - 1$.

the dicarbadodecaborane cage led to the formation of the new monocarbaborane framework. The primary aim of this work was to study the effects of substituents on this polyhedral cage geometry. Additionally, we wished to determine the position of the ethanol solvent molecule in the unit cell to try to explain why it was not possible to wash the C_2H_5OH from the title compound. The synthesis, chemistry and NMR spectra of this compound will be published elsewhere (Plešek, Jelínek, Štíbr, Heřmánek, Fontaine & Kennedy, 1990).

Experimental. Transparent colourless acicular crystal $0.1 \times 0.1 \times 0.5$ mm was mounted on a Hilger & Watts four-circle diffractometer; Mo $K\alpha$ radiation, Nb filter; cell parameters and standard deviations were obtained by least squares from 40 reflections ($5 < \theta < 20°$) (Shoemaker, 1970); 5606 unique independent reflections by learnt-profile method (Clegg, 1981) measured by $\theta/2\theta$ scans to $\sin\theta/\lambda = 0.595$ Å^{-1} for $h\,0\to12$, $k\,-12\to13$, $l\,-16\to16$. The 3982 reflections with $I > 1.96\sigma(I)$ were regarded as observed. Intensities of three standards ($3\bar{2}6$, 600, 080) were measured every 30 reflections, no signifi-

cant variation; data corrected for Lorentz and polarization effects, but not for absorption and extinction.

The structure was solved by direct methods using $MULTAN80$ (Main et al., 1980) and subsequent standard Fourier techniques. Full-matrix weighted least-squares refinement on F of all reflections with local version of $ORFLS$ (Petříček & Malý, 1981). Anisotropic temperature factors for 40 non-H atoms. All 40 H atoms were found from the difference Fourier synthesis and their x, y, z and individual isotropic temperature factors were refined. Function minimized $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$; in final cycle $R = 0.058$, $wR = 0.073$, $S = 1.37$ (for observed reflections), average $\Delta/\sigma = 0.01$, $(\Delta/\sigma)_{max} = 0.05$; max. and min. peak heights in final difference Fourier synthesis $+0.33$ and -0.30 e Å^{-3}. Scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV). Calculations performed on a Siemens 7536 computer. Figures were prepared using the program $PLUTO$ (Motherwell & Clegg, 1978).

Discussion. Final atom coordinates are given in Table 1; bond lengths for non-H atoms, some torsion angles and hydrogen interactions are summarized in

Table 2.* The structure consists of a tetraphenyl-phosphine cation and a monocarbaborane cage anion where methyl and OH groups replace two terminal H atoms of B8 and B9 in the polyhedral cage. The structure also contains one molecule of ethanol solvent. A view of two anions and two ethanols connected with hydrogen bonds about a centre of symmetry is shown in Fig. 1 together with the numbering scheme.

The nine B atoms and one C atom form a carba-nido-decaborane cage with mean B—B = 1·787 (5) Å. The C atom is placed in the 6 position and has mean C6—B = 1·576 (5) Å. The CH_3 group is attached on the other side of the cage to B9 with B—C = 1·569 (7) Å. The OH ligand, bonded to B8 [B—O = 1·406 (4) Å], forms a centrosymmetric hydrogen-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances involving H atoms and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53134 (67 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
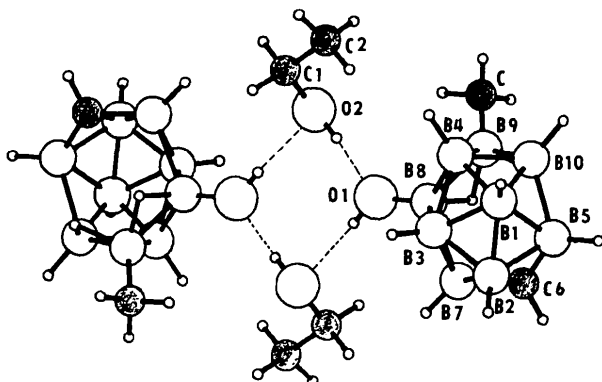

Fig. 1. Hydrogen bonds (dashed lines) between two anions and two ethanols with the atom-numbering scheme.
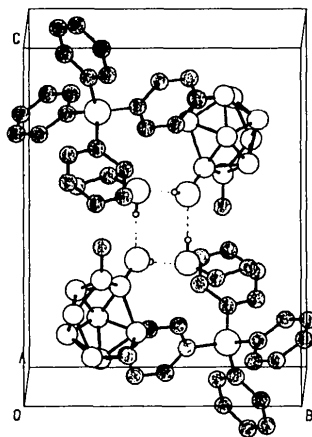

Fig. 2. Contents of the unit cell (H atoms omitted).

bonded dimer (Fig. 1, Table 2d) via the solvent ethanol. The O···O distances are clearly within normal ranges for this interaction (Brown, 1976). This explains why the structural stability of the ethanol solvent is stronger here than in some other examples (Mackay, Sadek & Culvenor, 1984; Ehrlich, Fronczek, Watkins, Newkome & Hager, 1984; Foces-Foces, Cano & Garcia-Blanco, 1983) and why the temperature factors of the non-H atoms in ethanol are reasonably low. The rigid hydrogen-bond framework probably also explains the impossibility of washing the ethanol solvate from this substance (Plešek, Jelínek, Štibr, Heřmánek, Fontaine & Kennedy, 1990).

Average distances of B atoms to their terminal H atoms in the carbaborane cage are B—H = 1·12 (4), and C—H = 1·02 (3) Å. The H_b atoms in the open part of the carbaborane cage form two bridges: B8—H_b(8,9)—B9 = 87·6 (16) and B9—H_b(9,10)—B(10) = 89·3(18)°, B8—H_b(8,9) = 1·31 (3), B9—H_b(8,9) = 1·27 (3), B9—H_b(9,10) = 1·36 (3) and B10—H_b(9,10) = 1·18 (3) Å.

The distances and angles in the PPh_4 cation [mean P—C = 1·792 (3), mean C—C = 1·379 (4) Å, C—P—C angles in the range 106·5–111·6°] are normal by comparison with other structures (Bates & Waters, 1985). The packing of the molecules in the unit cell is illustrated in Fig. 2.

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